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13. ABSTRACT (Maximum 200 words)

The Minority Institution ARO Fuel Cell/Battery/Manufacturing Hub at IIT ("Hub") focused during its six-year activity on three tasks. Task 1 concerned fuel cell and fuel cell manufacturing research, specifically concentrated on the direct methanol fuel cell (DMFC); (2) high-energy rechargeable battery research concentrated on Li-ion batteries; (3) minority outreach to give undergraduate minority students hands-on experience in electrochemical energy conversion technology and attract them to graduate studies. IIT acted as the lead institution for a consortium including five major research universities, a national lab, and two small companies, as well as three minority institution universities. The research function produced five patent or patent applications and more than 25 articles in refereed journals. These papers report results in DMFC performance, fuel cell and electro-organic electrocatalysis, combinatorial methods for catalyst discovery, molecular modeling of electrocatalytic mechanisms, synthesis of novel lithium-battery materials, and thermal characterization of Li-ion batteries. A specially structured minority outreach program gave 40 students hands-on experience, of which nine continued to graduate studies.

14. SUBJECT TERMS DMFC, direct methanol fuel cell, fuel cell, electrocatalysis, Pt alloy catalyst, electro-organic catalysis, combinatorial methods, molecular modeling, density functional theory, Li-ion cell, thermal run-away, thermal management of batteries, ARC, electrochemical calorimetry, minority outreach, Hub	15. NUMBER OF PAGES 14
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Minority Institution
ARO Fuel Cell/Battery Manufacturing Research Hub

1. Overall Objectives and Mode of Operation

The overall objectives of the ARO Hub program were two-fold: (1) to develop a multi-institutional center of coordinated graduate research in fuel cell and battery research, including manufacturing research; and (2) to expose undergraduate minority students to this emerging field of electrochemical energy conversion. IIT acted as the lead institution of the Hub, coordinating the efforts of a consortium that included, over the course of the program, twelve partners. The research partners included Argonne National Laboratory, several major research universities, and several small companies involved in fuel cell and battery development. The minority institution (MI) partners were three MI universities. The funds provided by ARO under the Hub program were used to establish teaching and/or research programs at IIT and at the partner locations. The MI partners familiarized undergraduate students with fuel cell and battery technology in Hub-sponsored undergraduate courses and laboratories. Qualifying minority students had the opportunity to take part in summer internships at IIT and its research partners. They also received fellowships to complete their study while continuing to do Hub-related research. The research partners participated in the minority outreach program by supervising minority students during the summer internship program. As technical research needs of the Hub collaboration changed, the outreach objectives remained the same.

2. Overall Accomplishments and Outcomes

The activities of the Hub were organized in three tasks: (1) Minority Outreach Task; (2) Fuel Cell Research Task; (3) Battery Research Task. Major accomplishments of these three tasks are summarized in the corresponding sections of this report.

Beyond the immediate goals and accomplishments under these Tasks, the Hub has had several important outcomes. At IIT, the Hub program led to the formation of the Center for Electrochemical Science and Engineering (CESE), directed by J. R. Selman. ARO funds were used to help establish a third electrochemical faculty line in IIT's Chemical and Environmental Engineering Department. This made it possible for J. Prakash to join IIT (from Energizer Inc.) in 1998. He is currently focusing on battery research.

The ARO program funds served as seed money for further fuel cell and battery projects. This has made it possible to attract, among others, UOP as a major contributor of funds to CESE activities. A commercial venture, NuVant Systems LLC, which grew out of the Hub-funded fuel cell research, focuses on commercialization of portable power systems based on DMFCs.

Last but not least, the Hub's unique outreach program identified and worked closely with 40 student participants from three MI partners, resulting in the continuation of a number of these students as graduate students in various schools. One of the Hub alumni (R. Cantu, UT Pan-Am) recently received his Ph.D. from the University of Houston in electrochemistry. IIT has also developed a continuing collaborative effort with Chicago State University.

3. Task 1: Minority Outreach

This task was the joint responsibility of the P.I.'s J.Robert Selman and Eugene S. Smotkin. A large part of the administration of this task was carried out by Ms. Bobbie Davis, Administrative Research Associate at IIT.

3.1. MI Partners and P.I.'s:

(1) Central State University (Wilberforce, OH):

P.I.: Dr. Vijay Gupta (1994-1997), Dr. Michael May (1997-1998)

(2) Chicago State University (Chicago, IL):

P.I. Dr. Justin Akujieze (1994-2000)

(3) Univ. of Texas-PanAmerican (Edinburgh, TX):

P.I. Dr. Deig Sandoval (1994-1997),

Dr. Roberto Gregorius and Dr. Hashim Mahdi (1997-2000)

3.2.Objectives:

- Develop electrochemical teaching laboratories at the three MI partners,
- Stimulate interest in applied electrochemistry at these institutions,
- Identify suitable candidates for summer internships under the Hub program;
- Provide financial support from Hub funding in the form of scholarships.

The summer internships aimed to expose minority students to graduate-level research by involving them hands-on in the research programs of IIT and its Hub research partners. Summer internships were organized by IIT, in cooperation with the partners, during five consecutive summers.

3.3. Major Accomplishments

At the start of the Hub program, each of the three participating MIs was provided with a complete set of basic equipment for a teaching laboratory in electrochemical and fuel cell/battery technology. Each MI supplemented this with specific equipment purchased from Hub sub-contract funds. A special undergraduate course in Electrochemistry of Fuel Cells and Batteries, with a laboratory using the Hub-funded equipment, has been taught at three institutions from 1995 to 1998. Since 1998, the same course content continues to be taught at Chicago State University and UT-PanAm, in the form of an individual tutorial. Successful completion of the course/laboratory and strong recommendations by the tutoring staff were prerequisites for a Hub Summer Internship. Successful completion of the internship generally was a prerequisite for a Tuition/Stipend Scholarship during the following academic year.

3.4. Summer Internships

Five internships were organized under the Hub program, in cooperation with the research partners Argonne National Laboratory (ANL), University of Minnesota (UMN), RBI Corporation (RBI) of Middleton, WI, and Pennsylvania State University (Penn State):

- Summer 1995 at IIT, ANL, UMN (8 students)
- Summer 1996 at IIT, ANL, UMN, RBI (10 students)
- Summer 1997 at IIT, ANL, UMN (10 students)
- Summer 1998 at IIT, ANL, UMN (12 students)
- Summer 1999 at IIT, ANL, UMN, and Penn State (7 students)

Several students participated in two consecutive summer internships.

3.5.Tuition/Stipend Scholarships

Of the 40 students participating in the Summer Internships, 36 received a scholarship partially covering tuition and stipend (totaling $6,400) in the academic year following the Summer Internship.

3.6. Continuation to Graduate School

Nine participants in the Minority Outreach program, after completing undergraduate studies, continued to graduate studies in science and engineering:

- From Central State University:

  Georges Edon (Kettering U., Flint, MI),

  Phalali Motsoetsoe (Capetown U., South Africa), Karen Hounsokou (I.I.T., Chicago)

- From University of Texas PanAmerican:

  Ricardo Cantu (U.Houston, TX),

- From Chicago State University:

  Tony Cochrane (Louisiana State U.),

  Nicole Scarbrough (U. of Wisconsin),

  Cheryl Tolbert (Virginia Polytechnic U.),

  Cynthia Akuleh (U. Michigan),

  Fontain Griffin (I.I.T.).

4. Task 2: Fuel Cell Research

This task was the responsibility of Eugene S. Smotkin, Hub P.I.

4.1. Participants and P.I.'s

(1) Illinois Institute of Technology, Chicago, IL (IIT) P.I. Eugene S. Smotkin

(2) University of Illinois, Urbana, IL (UIUC) P.I. Andrzej Wieckowski

(3) Pennsylvania State University, University Park, PA (Penn State) P.I. Thomas E. Mallouk

(4) California Institute of Technology, Pasadena, CA (CalTech) P.I. William Goddard III

(5) Columbia University, New York City, NY P.I. Richard Friesner

(6) ICET Inc. Norwood, MA P.I. Srinivasan Sarangapani

Initially, Argonne National Laboratory also participated in the Fuel Cell Task.

4.2.Objectives

The objectives of the ARO fuel cell program, initially focused on DMFC technology, broadened over time to develop a comprehensive program in fuel cell catalysis including:

(1) ab initio quantum mechanical modeling,

(2) discovery and synthesis of catalysts,

(3) testing of catalysts in half-cells and in full fuel cells,

(4) *in-situ* spectroscopic analysis of fuel cell membrane electrode assembly (MEA) surfaces,

(5) fundamental studies on real catalytic and model surfaces.

4.3. Major Accomplishments

(1) Role of formic acid in DMFC

At UIUC, the Wieckowski group examined *formic acid* decomposition as a probe of the catalytic properties of Pt and palladized Pt electrodes. The rate of formic acid oxidation on Pt/Pd is at least two orders of magnitude higher than that of methanol oxidation on Pt/Ru catalyst. If methanol could be reformed internally to formic acid in a fuel cell, the electric efficiency would easily match that of a hydrogen-fed fuel cell. The decomposition reaction of formic acid involves several elementary processes. The primary step is the oxidation of formic acid to an unstable surface intermediate COOH. The COOH species must also be formed when CO, generated from methanol on a Pt/Ru catalyst, is oxidized to CO_2. An *in situ* spectroscopic scrutiny of such a transient species may throw new light on methanol reactivity on catalytic electrodes. Work is continuing in that area at UIUC and IIT.

(2) MEA surface spectroscopy

At IIT both polarization modulated infrared reflection-absorption spectroscopy (PM-IRAS) and diffuse reflection spectroscopy are used to study smooth surfaces and MEA surfaces, respectively. The IIT group has established itself as a leader in the field of *in-situ* spectroscopy of fuel cell MEA's (Figure 1). The diffuse reflectance spectroscopy has been focused on methanol/water vapor fuel cells. The group's recent paper in the J. Phys.Chem. (Ref.14 of Section 6.2.(1)) demonstrates a phenomenon of increased reflectivity due to adsorbed CO on Pt particles supported on Nafion. Inverted bipolar peaks are mentioned more frequently in the literature and have been ascribed to contact of the Pt particles to moderately electronically conducting supports. Nafion is an electronic insulator, thus there are fundamental issues in specular reflectance yet to be developed. In addition to reflectance studies of high surface area fuel cell electrodes, the IIT group has demonstrated excellence in the use of PM-IRAS of model alloy surfaces. This work has been complimented by potential dependent XPS conducted at UIUC in the Wieckowski group. The IIT group was the first to confirm the formation of esters in gas-fed DMFCs by FTIR of real world MEAs.

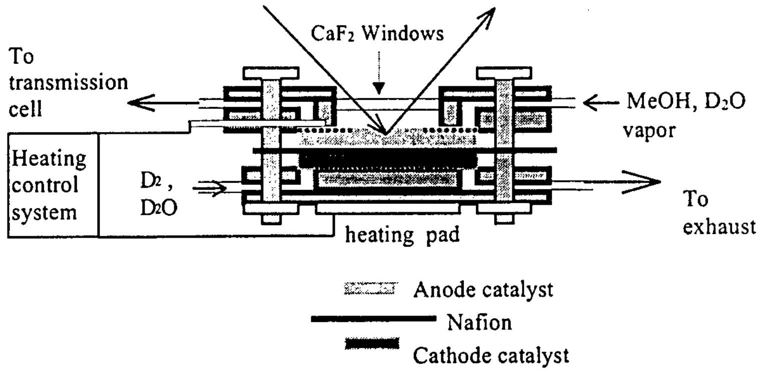
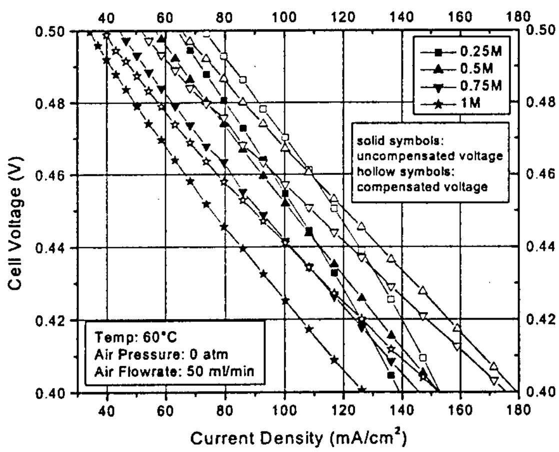
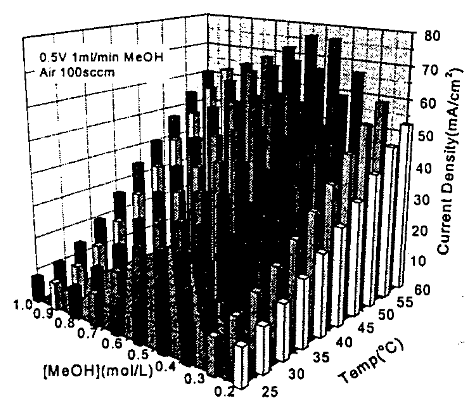


Figure 3. Direct methanol fuel cell for FTIR spectroscopy.

(3) DMFC performance.

Single cell DMFC cell performance at IIT is outstanding. The left side of Figure 2 (below) shows both compensated and uncompensated polarization data at 60°C, with air as oxidant, at zero gage





pressure for both electrodes. These data are being utilized by NuVant Systems for design of Palm Power DMFCs. The right side of Figure 2 shows the performance versus temperature from ambient to 60°C. These data are essential since the DMFC-powered laptop computer will operate between 45 and 60°C to facilitate heat rejection.

(4) New insights in the mechanism of methanol oxidation.

The widely accepted mechanism for methanol oxidation on Pt based catalyst surfaces has held that the rate determining step is activation of water, and/or oxidation of surface-bound CO to CO_2. In this view, enhancement of the water activation kinetics on Pt is the main function of oxophilic transition metal promoters including Ru, W and Sn. For decades the search for improved methanol oxidation electrocatalysts has focused on water activation. A systematic deuterium isotope study, conducted at IIT, has established that the rate-limiting step in methanol oxidation is potential dependent. At potentials relevant to DMFC operation, C-H bond activation is rate limiting on mixed metal catalysts based on Pt and Ru. Thus the search strategy for Pt promoter metals should focus on consideration of C-H activation, since water activation by Ru is adequate. This work has been submitted for publication to *Science*.

(5) Density functional theory calculations.

Density functional theory calculations have been published for 13 intermediate structures in methanol oxidation by Goddard (CalTech). IIT has nearly completed a systematic set of calculations of CO stretching frequencies on Pt clusters from 4 to 21 atoms. In collaboration with the University of Puerto Rico we have published preliminary calculations on PtRu alloys.

(6) Combinatorial methods.

In collaboration with T. Mallouk (Penn State), combinatorial methods have been developed for the discovery of new materials ranging from zeolites to heterogeneous catalysts, including heterogeneous catalysts. We have developed a rapid combinatorial synthesis and screening method for the discovery of new electrocatalysts, published in *Science* (Ref.8 of Section 6.2.(1)). Superior catalysts have been discovered in three major areas:

- Quaternary catalysts (PtRuIrOs) have been discovered for methanol electrooxidation that are superior to PtRu, especially at higher concentrations (> 1 molar).
- An enzyme free catalyst has been discovered that oxidizes glucose near the thermodynamic potential. A patent on the use of this catalyst in amperometric glucose sensors is pending. Interference from ascorbate, urate, and other reducing agents found in serum or blood can be largely eliminated by operating the sensor at potentials negative of -500 mV vs. MSE.
- Polymer electrolyte membrane (PEM) regenerative cells that can perform both as a fuel cell and an electrolyzer promise to be very efficient energy conversion and storage devices for both space and terrestrial applications. These systems usually have one electrode for oxygen evolution and reduction, and another electrode for the corresponding hydrogen reactions. With favorable kinetics at the hydrogen electrode, the key issue in these systems is the development of more active and stable bifunctional catalysts for the oxygen electrode. A combinatorial method has been applied to this problem. A 715-member electrode array containing five elements was fabricated by a robotic plotter. The array was then conditioned at high current density and screened for the most corrosion resisting and active catalysts. Both oxygen evolution and reduction have been screened for, by converting the protons generated or consumed in the electrochemical half-cell reactions to a fluorescence signal using an

indicator. The most active compositions identified for dual use were further tested and characterized.

4.4. New Research Directions

The combinatorial methods developed in the ARO Hub program are now being extended to heterogeneous catalysis in general. Penn State and IIT have collaborated with UOP (Des Plaines, IL) in a $30 million dollar NIST ATP proposal for discovery of water-gas-shift catalysts and dehydrogenation catalysts. In addition, a seed grant was provided by UOP for the discovery of reformate air fuel cell electrocatalysts. The new combinatorial methods are now being applied to catalysts for chemical sensors in medical and process control systems.

A new area of electrochemistry was developed within the ARO Hub program and has been described in JACS (Ref.6 of Section 6.2(1)) and more recently in a paper in Solid State Ionics (Ref.15 of Section 6.2.(1)). This area is related to, but different from, the work of Vayenas in promotion of non-Faradaic reactions by electrochemical modification of catalytic activity (NEMCA). At IIT we have shown that non-Faradaic isomerization reactions of alkenes are potentially modulated by a hydrogen spillover mechanism. We elucidated the mechanism of electrochemical isomerization reactions using isotope effect studies, mass spectroscopy and FTIR. We are continuing a strong effort in this area.

4.5. New Opportunities

A new company, NuVant Systems LLC, has been formed to promote the results of the HUB fuel cell effort. NuVant founders include, from the Hub program, T. Mallouk (Penn State), E. S. Smotkin (IIT), and S. Sarangapani (ICET Inc.). IIT and NuVant have signed a contract to facilitate the commercialization of intellectual property and know-how developed during the Hub program as well as in post-Hub research. The focus of the company is the development of portable power systems based on DMFCs. NuVant Systems is developing turnkey systems for laptop computers and other small electronics. In addition to venture capital funders, companies such as W. L. Gore and UOP have expressed interest in NuVant Systems. IIT has submitted an STTR grant proposal in collaboration with ICET Inc. and NuVant Systems.

4.6. Future Needs

The academic/industrial consortium developed during the Hub program is continuing to work in a collaborative effort towards the development of practical DMFCs. The fuel cell consortium developed within the ARO Hub program is a true soup-to-nuts program that encompasses a range of focus from ab initio density functional theory calculations to design of systems (NuVant Systems, LLC). The broad range of fundamental and practical goals requires funding from government agencies as well as industrial partners to continue this very productive collaborative effort.

5. Task 3: Battery Research

This task was the responsibility of J.Robert Selman, Hub-P.I.

5.1. Participants and P.I.s

(1) Illinois Institute of Technology, Chicago, IL (IIT) P.I.: J. Robert Selman

(2) University of Minnesota, Minneapolis, MN (UMN) P.I.: William H. Smyrl

(3) Argonne National Laboratory, Argonne, IL (ANL) P.I. Donald R. Vissers, Andrew Jansen

(4) RBI Corporation, Middleton, WI (RBI) P.I. Sid Megahed (1994-1997)

Initially Rayovac Corporation (Madison, WI) was involved in the Hub. Its place was taken by RBI Corporation when S. Megahed moved to RBI. RBI's involvement ceased with his death in 1997. IIT, UMN, and ANL have been involved in the Hub from beginning to end.

5.2. Objectives

(1) Develop and apply electrochemical-calorimetric characterization methods for the study of advanced rechargeable batteries;

(2) Study the performance and stability of metal hydride electrodes in nickel/metal hydride batteries;

(3) Study processing effects on the synthesis and electrochemical behavior of anode and cathode materials for lithium-ion batteries.

5.3. Major Accomplishments

(1) Electrochemical-calorimetric characterization of Li-ion batteries.

The IIT group developed the experimental apparatus and procedures to carry out such measurements for an entire charge/discharge cycle, and establish both the reversible (chemical) and irreversible (polarization-dependent) component of the heat effect. For the first time, systematic measurements were made on Li-ion batteries, under normal and abusive conditions, and the results used to predict the temperature sensitivity of scaled-up batteries. This research took place in several stages:

(a) The Accelerating Rate Calorimeter (ARC) developed for testing of explosives was adapted to battery cycling (using an Arbin cycler), and various monitoring methods were worked out. A schematic of the set-up is shown in Figure 3.

(b) Heat generation rates at different discharge rates and operating temperatures were measured for commercial Li-ion batteries. The IIT battery group was the first to report the significant reversible (entropic) heat effect of Li-ion batteries containing lithium cobaltite as cathode material. Under normal operating conditions, this effect accounts for 40-60% of the total heat generation. Prior to this work such reversible heat effects were often neglected, due to lack of information. Thiese results have been reported in J. Electrochem. Soc. and J. Power Sources (Ref.. 3, 6, and 7 of Section 6.2.(2)).

(c) These heat generation rates and other thermal property data reported by the IIT battery group provide a firm basis for thermal performance modeling of scaled-up Li-ion batteries. Simulation results for large-scale batteries of 10-100 A-hr capacity have been reported in J. Power Sources (Ref. 4 of Section 6.2 (2))

(d) The galvanostatic intermittent titration technique (GITT) has been applied to correlate electrochemical-calorimetric characteristics with structural changes upon lithiation/delithiation in commercial lithium-ion cells. The IIT battery group first derived a phase diagram for the cathode material from calorimetric measurements as a function of lithium concentration (x) in the host material. The result agrees well with phase diagrams by structural characterization. (Refs. 8 and 9 of Section 6.2.(2))

(e) The onset-of-thermal-runaway (OTR) temperatures for commercial Li-ion cells and their component materials have been measured, as shown in Fig.4, below (reported in J. Power Sources, Ref. 4 of Section 6.2.(2)). The measured open circuit voltage drops sharply during the thermal runaway reaction, indicating an internal short circuit at temperatures between 145-150 °C for all open circuit voltages.

(2) Performance and stability of metal hydride electrodes.

The effect of Al and Mn doping on long-term cycling performance was studied by Argonne National Laboratory in cooperation with IIT. In-cell neutron diffraction measurements were carried out by means of a specially constructed cell directly exposed to ANL's Intense Pulsed Neutron Source. The results (Ref. 1 of Section 6.2.(2)) suggest the advantages of studying multiple dopant effects using this same technique.

(3) Effect of processing on synthesis and electrochemical behavior of lithium-ion cell components.

The U. of Minnesota group carried out research on several kinds of intercalation oxides. The first group was vanadium pentoxide synthesized as high surface area powders and self-standing films through a variation of synthetic procedures. It was demonstrated that 2 equivalents of lithium may be inserted per atom of vandium. Studies on amorphous MnO_2 demonstrated that, in addition to the high lithium insertion capacity (two equivalents Li^+ per MnO_2), this material is capable of polyvalent cation (e.g. Al, Mg, and Zn) insertion at appreciable capacity.

5.4. New Research Directions

It has been demonstrated in our work that the heat generation rate of Li-ion batteries is a major challenge to the scale-up of these batteries for high-power applications such as mobile electronic command modules. Through the Hub program, the IIT battery group has developed a unique capability to characterize Li-ion battery chemistry rapidly. A simplified thermal model is now available as a design tool for scaled-up batteries. We are now investigating non-traditional thermal management techniques, and are in the process of constructing a large database of thermodynamic and thermal properties measurements on novel battery materials.

5.5. New Opportunities The IIT battery group, in collaboration with Argonne Laboratory and battery companies (including Rayovac Corporation), has started a project to measure thermodynamic properties of different cathode ($LiMnO_2$, $LiCoO_2$, and $LiNi_{0.8}Co_{0.2}O_2$) and anode materials (graphite, hard carbon, and graphitized carbon), as a function of composition and processing methods. This will provide the necessary empirical basis to underpin the development of fundamental methods for predicting the energetics of solid-state-ionic, metal alloy, and carbonaceous materials used in high-energy battery electrodes. Advances in molecular modeling techniques (such as crystal field density computations) will greatly help this endeavor.

5.6.Future Needs

The IIT battery team seeks a connection with groups experienced in molecular modeling techniques to develop semi-empirical modeling techniques at the meso-scale of electrode materials such as carbon and manganese oxide spinels. In addition, expanded capabilities in the synthesis area (ultra-high temperature furnaces, plasma reactors) are pursued, as well as connections with commercial microfabricators.

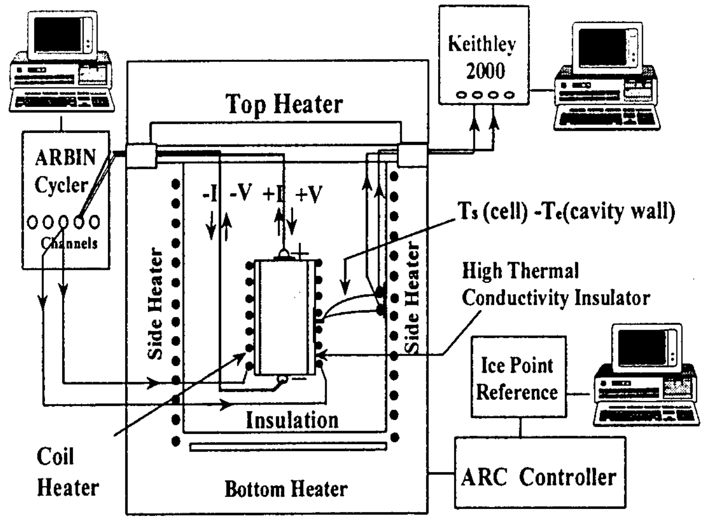


Fig.3: Experimental set-up of the ARC-Arbin experiments

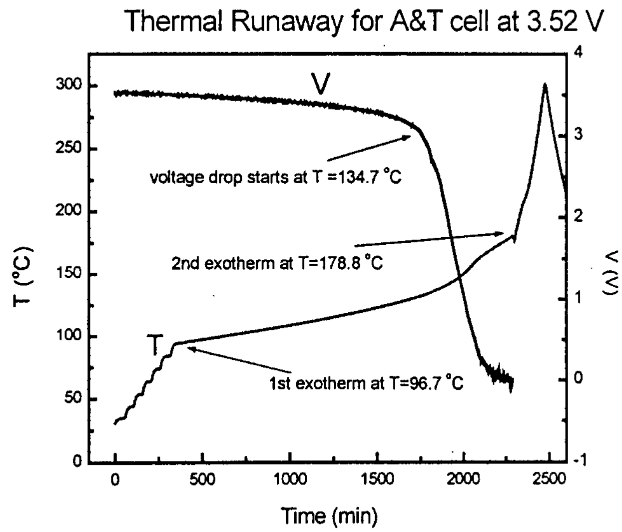


Fig.4: Thermal runaway experiment

6. Patents and Publications

6.1. Patents

(1) Patents Awarded

1. E. S. Smotkin, et al., “Hybrid Electrolyte System” U.S. Patent 5,846,669, Dec. 8, 1998
2. E. S. Smotkin, et al., “Single Phase Ternary Pt-Ru-Os Catalysts for Direct Oxidation FCs” U.S. Patent 5,856,036, January 5, 1999.

(2) Patent Applications Pending

1. T. E. Mallouk, E. S. Smotkin, B. C. Chan, E. Reddington, B. Gurau, R. Viswanathan, A. Sapienza, R. Liu, and G. Chen, "Electrocatalyst Compositions," U. S. Patent Application 09/326,206 (filed June 4, 1999).
2. T. E. Mallouk, E. S. Smotkin, E. Reddington, and A. Sapienza, "Method of Screening Compositions for Electrocatalytic Activity," U.S. Patent Application 09/326,205 (filed June 4, 1999).
3. T. E. Mallouk, B. C. Chan, E. Reddington, E. S. Smotkin, B. Gurau, R. Viswanathan, and R. Liu, "Ternary and Quaternary Electrocatalysts for Reformate-Air FCs," Penn State Invention Disclosure, December 31, 1998.

6.2. Refereed Journal Publications

(1) Fuel Cells

1. Cong Pu, Wenhua Huang, K. L. Ley and E. S. Smotkin, "A Methanol Impermeable Proton Conducting Composite Electrolyte System," *J. Electrochem. Soc.*, **142,** L119-L120 **(1995)**
2. Q. Fan, Cong Pu, K. L. Ley and E. S. Smotkin, "*In-Situ* FTIR-Diffuse Reflection Spectroscopy of the Anode Surface in a Direct Methanol/Oxygen Fuel Cell," *J. Electrochem. Soc.*, **143**, L21- L23 **(1996)**
3. Qinbai Fan, Cong Pu and E. S. Smotkin, "*In-Situ* FTIR-Diffuse Reflection Spectroscopy of Direct Methanol Fuel Cell Anodes and Cathodes," *J. Electrochem. Soc.*, **143,** 3053-3057 **(1996)**
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6. L. Ploense, Maria Salazar, Bogdan Gurau and E. S. Smotkin, "Proton Spillover Promoted Isomerization of n-Butylenes on Pd-Black Cathodes/Nafion 117," *J. Am. Chem. Soc.*, **119,** 11550-11551 **(1997)**
7. Li Liu, Cong Pu, Renxuan Liu, Qinbai Fan, E. S. Smotkin, "Carbon Supported Vs Unsupported Pt/Ru Anodes for Liquid Feed Methanol Fuel Cells;" *Electrochimica Acta,* **43,** 3657-3663 **(1998)**
8. E. Reddington, A. Sapienza, B. Gurau, R. Viswananthan, S. Sarangapani, E. S. Smotkin, T. E. Mallouk, "Combinatorial Electrochemistry: A Highly Parallel, Optical Screening Method for the Discovery of Better Electrocatalysts", *Science,* 280, 1735 - 1739 **(1998)**
9. L. Liu, R. Viswananthan, R. Liu, E.S. Smotkin, "Methanol Oxidation on Nafion Spin-Coated Polycrystalline Platinum and Platinum Alloys," *Electrochemical and Solid-State Lett., 3,* 123-125 **(1998)**
10. Bogdan Gurau, Ramesh Viswananthan, Renxuan Liu, Todd J. Lafrenz, Kevin L. Ley, and E. S. Smotkin, "Structural and Electrochemical Characterization of Binary, Ternary, and Quaternary Platinum Alloy Catalysts for Methanol Electro-oxidation," *J. Phys. Chem. B,* 102, 9997-10003, **(1998)**
11. B. K. Mandal, C. J. Walsh, T. Sooksimuang, S. J. Behroozi, Sangu-gu Kim, Yong-Tae Kim, E. S. Smotkin, R. F. Filler and Cathy Castro, "New Class of Single Ion-Conducting Solid Polymer Electrolytes Derived from Polyphenols" *Chemistry of Materials,* **12,** 6-8, **(2000)**
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